

PET

**Recycling Concepts
for Polyester**

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1. Introduction

Polymer recycling always means that the polymeric material was already transformed, somehow, into a semi-finished product or an end product and that it is produced during the processing phase or after being used, or that it is gathered as a material so that it can be led back to the production of polymeric semi-finished products or polymeric products. When recycling, two ways generally have to be differentiated. The chemical transformation into initial raw materials, the polymer structure being destroyed, and the physical treatment, the initial polymer properties being maintained or reconstituted.

With polyester, raw material recycling leads to terephthalic acid or dimethyl terephthalate and ethylene glycol; with polyamide 6, it leads to caprolactam. These recycling processes only prove to be cost-efficient with big lines > 50,000 tons/year and are still an exception today. Such lines could only be seen, hitherto, in the production centres of big producers like Eastman, DuPont or KOSA.

Direct circulation in a polymeric state is today operated in the most diverse variants; the processes used for this are typical of the medium-sized industry, and cost-efficiency can already be achieved with line sizes of approx. 10,000 tons/year. In this case, all forms of recycled-material feedback into the material circulation are possible, the recycling process PET-bottle back to the bottle, for example, being a rather special case. Hereafter, the diverse recycling processes - in particular regarding the decontamination of foreign substances - are being checked, the filtration of polymeric melts and intermediate products playing a particular part. Besides the chemical deposits and degradation products, mechanical deposits represent the main part of depreciating additions. Due to the trend that recycled materials are increasingly introduced into manufacturing processes, which were originally designed for new materials only, an efficient filtration becomes more and more important. In recycling, the filtration process has to meet - compared with traditional filtration - the following demands in polymer manufacture:

- # Coping with a very wide granular size spectrum and material spectrum
- # Coping with very high, stochastically appearing contamination during process-constant and fully-automatic operation
- # Shortest dwell-time of the dirt cake in the melt
- # Fine filtration (20 - 50 μm)

With regard to equipment, it is the Rotary Filtration Systems of the company Gneuß Kunststofftechnik - which operate automatically and pressure-constantly - that meet all of these demands best currently.

2. Fundamental principles

The number of defects which accumulate in the polymeric material is permanently increasing - when processing as well as when using polymers - taking into account a growing service life and repeated processing. As far as polyester is concerned, the defects mentioned can be found in the following groups:

Reactive end groups are transformed into dead, i.e. not reactive end groups, e.g. formation of vinyl ester end groups through dehydration or decarboxylation of terephthalate acid, reaction of the COOH or OH end groups with mono-functional degradation products.

Decrease in reactivity, widening of the molecular weight distribution.

The end group proportion shifts in the direction of the COOH end groups built up through a thermal and oxydative degradation.

Decrease in reactivity, increase in the acid autocatalysis in the thermal degradation in the presence of humidity.

The number of polyfunctional macromolecules increases.

Accumulation of gelation and of the long-chain branching.

The number, the size and the variety of not polymer-identical organic and inorganic foreign substances increase.

With every new thermal stress, the organic foreign substances react by decomposing, this causing the liberation of further degradation-supporting substances and colouring bodies.

Due to service life in the presence of air and humidity, as well as to the influence of ultraviolet light, hydroperoxide groups build up on the polymer surface; during an ulterior treatment process, they work as a source of oxygen-radicals.

The destruction of the hydroperoxides is to happen before the first treatment or during plasticisation and can occur with suitable additives.

Under the conditions mentioned above, there is a modification of the following measurable characteristic values, in particular, i.e.:

Rise in the COOH end groups

Rise in the dye number b

Rise in haze (with clear products)

Rise in the content of oligomers

Rise in the filter value

Rise in the content of by-products such as acetaldehyde, formaldehyde

Decrease in the dye colour L

Decrease in the IV or the dynamic viscosity

Decrease in crystallisation temperature and increase in crystallisation speed

Decrease in the mechanical strength

Widening of the molecular weight distribution

3. Decontamination as an important processing step in recycling

The success of any recycling concept lies in the efficiency of decontamination in the right place in processing and to the necessary extent. Generally, the following applies: the sooner foreign substances are removed, in the process, and the more thoroughly this is done, the more efficient the process is. The high plasticisation temperatures of PET are the reason why almost all common organic deposits such as PVC, chemical woodpulp and paper fibres, polyvinylacetate, melt adhesive, colouring agents and protein residues are transformed into coloured degradation products which, in their turn, release reactive degradation products.

The number of defects in the polymer chain then increases considerably. Naturally, the particle size distribution field is very wide, the big particles of $> 60 \mu\text{m}$ - which are visible and easy to filtrate - representing the lesser evil since their total surface is relatively small and the degradation speed is therefore lower. The influence of the microscopic particles, which - if they are many - increase the frequency of defects in the polymer, is much bigger.

According to the motto "What the eye does not see the heart cannot grieve over", it is, still today, considered to be very important - in many recycling processes - to remove the mainly visible deposits, the used filtration processes playing a particular part in this case.

4. Processing examples for recycling to the initial raw materials

Glycolysis and partial glycolysis

In the field of glycolysis and partial glycolysis, the polyester which has to be recycled is transformed into an oligomer by adding ethylene glycol or other glycols. The aim and advantage of this way of processing is the possibility of parting the mechanical deposits - this system being directly connected to the glycolysis - through a progressive filtration; the filtration fineness of the last filtration step has a decisive effect on the quality of the end product.

The traditionally used candle filters or bolt screenchangers are not suitable for this way of processing since foreign substances remain for a certain time in the polymer flow, being considerably degraded and, furthermore, releasing degradation products in the glycolysate.

Only an automatically-operating filtration, which permanently provides clean filtration surface area and with which the filter cake is immediately and continuously removed from the melt flow, is especially suitable for such a process. What is also important, is that the amount of contamination, which strongly varies with recycled materials, can be coped with without any problem and automatically.

Taking partial recycling with partial glycolysis as an example, it is to be demonstrated how bottle waste can successfully be recycled in a discontinuously operating polyester line with which pellets for textile applications are manufactured.

The task consists in feeding 25% bottle flakes and maintaining at the same time the quality of the textile pellets which are manufactured on the line. This task is solved by degrading the bottle flakes - already during their first plasticisation which can be carried out in a single- or multiwave extruder - to an IV of approx. 0.30 dl/g by adding small quantities of ethylene glycol and by subjecting them to a fully-automatic fine filtration directly after plasticisation.

The daily output of the line amounts to 30 t with a batch size of 3.75 t so that the separate melt stream which has to be fed is of approx. 312 kg/h.

The filtration of a very wide granular size spectrum can make a progressive filtration necessary, coarse filtration of around 60 μm and fine filtration of around 6 μm operating directly one after the other. For simplification purposes, operation can also take place in one step, a corresponding graded design of the filter packages (e.g. 200 μm , 60 μm , 6 μm) being necessary. For this task, the continuously operating filtration system RSF*genius* is used. Furthermore, temperature is brought to the lowest possible limit. In addition, with this way of processing, the possibility of a chemical decontamination of the hydroperoxides is used by adding a corresponding P-combination directly when plasticising.

The destruction of the hydroperoxide groups is, with other processes, already carried out during the last step of flake treatment.

The partially glycolysed and finely filtered recycled material is continuously fed to the esterification reactor, the dosing quantities of the raw materials being adjusted accordingly.

The treatment of polyester waste through glycolysis to bis-beta hydroxy-terephthalate, which crystallises and can be used, instead of DMT or PTA, as a raw material for polyester manufacture, has only existed on paper up to now. What also applies for such a process, which works at a processing temperature above 220°C, is that the deposits which can be filtered down to 3 μm have to be extracted from the process as soon as possible. With a line size of 50,000 tons/year there are, with such a processing concept, hourly outputs of > 6000 kg which also have to be treated with filters as described above.

Hydrolysis

Recycling processes, through hydrolysis of the PET to TPA and EG, work under high pressures in the supercritical area. In this case, PET-waste is directly hydrolysed, and it is only when the TPA is recrystallised to acetic acid that mechanical deposits can be removed. Large-scale lines on this basis have not been known to date.

Methanolysis

Methanolysis is the processing which has been practised and tested on a large scale for many years. In this case, polyester waste is transformed into DMT, under pressure, with catalysts and methanol, this making an efficient filtration of the methanolysis mix necessary after the methanolysis.

5. Processing examples for polymer recycling

Polymer recycling processes with polyester are almost as varied as the manufacturing processes of primary pellets.

Besides BOPET-film for video and audio films and other special applications, e.g. smooth yarns through FDY-spinning at > 6000 m/min or microfilaments and microfibrils, of which the manufacturing processes are very strongly connected with the purity of the basic polymer, recycled materials can today be used in all manufacturing processes.

The fact that some machine manufacturers and line builders in Europe make efforts to offer independent recycling processes, e.g. for the treatment of PET-bottles, such as EREMA, OHL or BÜHLER, aims at generally furnishing proof of the "existence" of the required extraction residues and of the removal of model contaminants according to FDA, which is necessary for the application of the treated polyester in the food sector. This is to certify the general suitability of the process control which has been chosen. Besides this process approval it is nevertheless necessary that any user of such processes has to constantly check the FDA-limits for the raw materials manufactured by himself for the process he is running.

6. Processes with regard to PET-recycling

a) Simple repelletizing of bottle waste

This process consists in transforming bottle waste into flakes, in drying and crystallising the flakes, in plasticising and filtering, as well as in pelletizing.

Product: amorphous regranulates of an IV in the range of 0.55 - 0.7 dl/g, depending on how complicated predrying is.

Special feature: acetaldehyde and oligomers are contained in the pellets; the viscosity is low, the pellets are amorphous and have to be crystallised and dried before further treatment.

Processing to spinning non-wovens, fibres, filaments, simple A-PET film, packaging film, SSP.

b) Manufacture of PET-pellets for bottles and A-PET

This process is, in principle, similar to the one described above; however, the pellets produced are directly (continuously or discontinuously) crystallised and then subjected to a solid state polycondensation (SSP) in a tumbling drier or a tube reactor. During this processing step, the corresponding IV of 0.80 dl/g is set again and, at the same time, the acetaldehyde content is reduced to < 1ppm.

c) Direct recycling of bottle flakes e.g. to pre-moulded articles and A-PET sheet

In order to save costs, one is working on the direct use of the PET-flakes, from the treatment of used drinks bottles, with a view to manufacturing pre-moulded articles and, too, A-PET sheet. For the adjustment of the necessary IV, besides an efficient drying of the flakes, it is possibly necessary to also reconstitute the IV through polycondensation in the melt phase or solid state polycondensation of the flakes.

For all processing variants, the basic condition is an efficient filtration of the melt which should in any case be carried out by means of a filtration system operating cost-efficiently and fully automatically with constant process conditions, at least down to 6 μm . The filter equipment RSF*genius* of Gneuß Kunststofftechnik GmbH for instance meets all these requirements.

d) Direct recycling in spinning process

When spinning regranulates or using directly secondary materials such as bottle flakes in spinning processes, there are a few processing principles.

High speed spinning processes for the manufacture of POY normally need a spinning IV of 0.62 - 0.64 dl/g. Starting from bottle flakes, the IV can be set via the degree of drying. The additional use of TiO₂-masterbatch is necessary for a full dull or semi dull polish. In order for the spinnerets to be protected, an efficient filtration of the melt is, in any case, necessary.

Staple fibres are spun in an IV-range which rather lies somewhat lower and which should be between 0.58 dl/g and 0.62 dl/g. In this case, too, the required IV can be adjusted via drying. For adjusting the IV, however, an addition of low-molecular recycled material can also be used.

In order to maintain the life of the spinpacks within reasonable limits, an efficient filtration is also necessary when spinning to obtain fibres.

Spinning non-wovens - in the fine titer field for textile applications as well as heavy spinning non-wovens as basic materials e.g. for roof covers or in road building - can be manufactured by spinning bottle flakes. The spinning IV, which has to be adjusted lies, with this process too, in the range of 0.64 dl/g. As is the case with the other spinning processes, the die packages can only be protected against too quick contamination through an efficient filtration.

For all spinning processes it is important that the filtration systems which are connected before the spinpack operate pressure- and process-constantly, that their filtration fineness is lower than that of the spinpack and, for cost-efficiency reasons, that they operate fully automatically.

e) Direct recycling of high tenacity packaging stripes and monofilaments

A special field where recycled materials are used is the manufacture of high tenacity packaging stripes - and monofilaments. In both cases, the initial raw material is a recycled material which was polycondensated to an IV in the range of 1 - 1.5 dl/g via an SSP. High tenacity packaging stripes as well as monofilaments are then manufactured in the melt spinning process; the high tenacity packaging stripes maintain their strength, this being due to the high drawing (similarly to technical yarns), and the monofilaments - which can for example be transformed into wire-mesh fence - get the suitable mechanical strength, this being due to the high IV in the monofilament. With such processes, filtration is limited to a separation of foreign substances $> 70 \mu\text{m}$.

f) Direct recycling of engineering plastics

When using recycled materials for the manufacture of injection-moulding compounds, only a coarse filtration of the melt is necessary (60 - 100 μm). When the recycled materials are filled with glass fibres, for example, filtration finenesses of $< 200 \mu\text{m}$ are not useful. For a continuously-constant quality, in this case too, the fully-automatic and pressure-constant filtration process represents a qualitative and cost-efficient advantage.

Summary

Considering the wide range of processes for recycling polyester, the decontamination steps which can be found in the different steps of the process are of particular importance. The following general principle applies: the sooner the decontaminants are removed, in the process, and the more thoroughly they are removed in the quantity the better the quality of the recycled material is. A further principle consists in removing the deposits quantitatively, if possible, before the first plasticisation since - due to the high melt temperature of polyester - most additions are strongly decomposed. The degradation products which are thus built up strongly damage the polyester, the colour and mechanical properties being particularly impaired.

For the filtration of polymer melts in recycling, the devices which are particularly suitable are those which guarantee a very short dwell-time of the dirt cake in the melt flow, while operating continuously and pressure-constantly, which can cope, without any problem, with the high deposits which often appear spasmodically, while operating automatically, and which guarantee process consistency.